Distribution of 1.68 eV emission from diamond films

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Free-standing polycrystalline chemical vapor deposition diamond films grown on a silicon wafer, with electrical behavior similar to values currently mentioned in the literature, present microheterogeneity. A detailed analysis by micro Raman shows how the diamond and nondiamond phases are distributed within the film and also the distribution of the silicon related luminescence. This luminescence is discussed in terms of two emitting centers close in energy. Absolute intensity of the diamond peak is not correlated with the good quality of the film as assessed by the Raman linewidth and ratio of this line to the nondiamond Raman lines. © *1998 American Institute of Physics.* [S0021-8979(98)08816-1]

I. INTRODUCTION

The chemical vapor deposition (CVD) growth of diamond films gives material with good mechanical and optical properties that approach those of bulk diamond.[1] However, there are some characteristics of diamond films that depend on the growth process, grain size, and dominant growth direction.[2] The quality of the diamond films is usually assessed by the width of the Raman line and the ratio between the diamond Raman line and the non-Raman lines.[3] Conductivity of the diamond films has been found to be higher than bulk insulating diamond although the nature of this conductivity is not well understood.[4]

A complex zero phonon line (ZPL) at 1.68 eV has been found in both Si-implanted and synthetic diamond doped with silicon. This system is well understood in bulk samples, and is attributed to an optical center corresponding to a silicon-vacancy defect (Si-*V*), where the Si occupies a position in the line joining two adjacent vacancies.[5] In the ZPL region 12 lines are found. The lines can be grouped in three groups of four lines, each group with an intensity proportional to the natural isotopic abundance of Si. This group of lines is due to transitions between a double split excited state to an also doubly split ground state. Nevertheless, the study of this emission in diamond films is more complex and different energy position, different phonon energies, and different de-excitation processes can be found in the literature. Peak positions for this emission are given as 1.675 and 1.680 eV;[6] 1.679 eV;[7] 1.681;[8] the doublet 1.6827 eV−1.6837 eV;[5] 1.685 eV,[9] and different thermal quenching parameters, 169 meV,[7] 70 meV,[8] and 56 meV[10] are found. This situation is due to the fact that in the polycrystalline films the lines are broader, losing the fine structure that is characteristic of the Si-*V* emission in bulk diamond. Usually this different peak position is attributed to internal stress. Even in the earlier reports the 1.68 eV center was considered as a distorted GR1 which is the neutral vacancy optical center in diamond.[6] However a clear distinction between this emission and GR1 has been established by the study of samples where both lines coexisted.[11] Also it was shown that this line even increased on thermal annealing at temperatures where neutral vacancies become mobile and are captured by point defects.[12]

In the present work we carried out a detailed analysis by micro-Raman and photoluminescence of free-standing diamond films grown on a silicon substrate, to study the dependence of the silicon related luminescence with the Raman film characteristics. The width of the line and the quality factor given by the ratio of diamond to nondiamond Raman lines has been studied in different regions of the sample, to understand the influence of the film characteristics in the luminescence. The luminescence studies are best interpreted based on the presence of two optical centers very close in energy.

II. EXPERIMENTAL DETAILS

Micro-Raman spectra were carried out by means of a Renishaw 2000 system, working with a He–Ne laser of 25 mW, which was focused on the sample to a spot size ~1 μm in diameter. Photoluminescence (PL) was excited with the 488 nm line of an Ar^+ laser, the sample being held in a cold tip of an Air-Products closed cycle He cryostat. The detection system comprises a SPEX 1704 monochromatic and a RCA C31034 photomultiplier. Current has been measured in both ac (complex impedance bridge: 1 kHz; 8 1/2 digits) and dc (electrometer: 10^{-15} A) regimes using aluminium contacts. Measurements of relaxation times were made using a square generator pulse with a rise time <100 ms.

Samples were free-standing light grey transparent 0.25 mm thick diamond films grown by microwave plasma chemical vapor deposition (MPCVD) in an ASTeX PDS 18 (2.45 GHz; 5 kW) and polished. From a scanning electron microscope (SEM) analysis an average grain size of 1.5–4 μm was estimated. Each sample was divided in six regions of 1.3 mm and the Raman spectrum was performed in the center of each region.

III. RESULTS AND DISCUSSION

Aluminium electrodes in a two terminal configuration were sputtered onto the sample, in order to measure electrical properties in both ac and dc regimes. Ohmic behavior has

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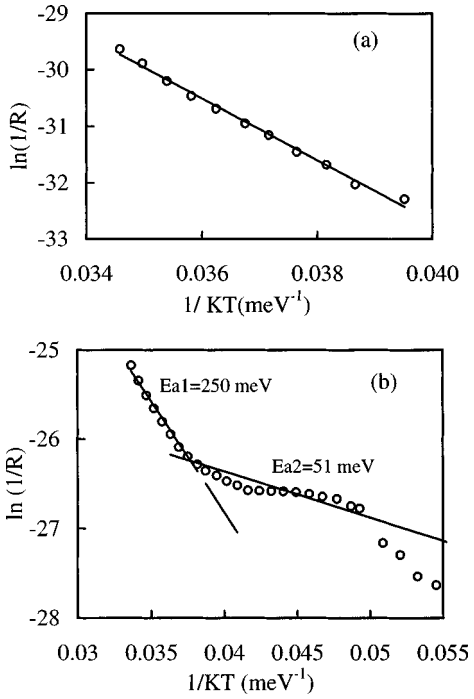

FIG. 1. The temperature dependence of reciprocal resistance: (a) dc measurements; (b) ac (1 kHz) measurements.

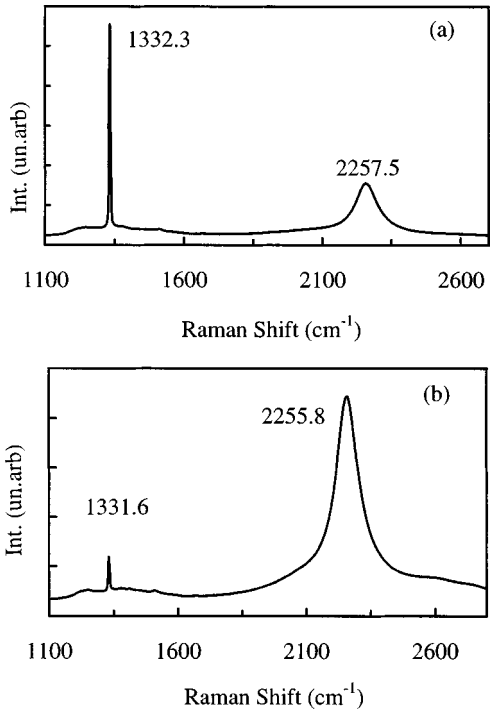

FIG. 2. Typical Raman room temperature spectra taken with He–Ne laser: (a) F-face; (b) D-face.

been found for dc conductivity below 310 K, but above this temperature a supralinear dependence was found, indicating the onset of semiconducting behavior. In Fig. 1 the temperature dependence of the reciprocal resistance is shown, where an Arrenhius behavior is observed with a correspondent activation energy of 545 meV. On the other hand, measurements in ac regime (1 kHz) show two activation energies of 51 and 250 meV. A model based in a distribution of activation energies can explain this lower value, which reflects in ac regime the lower path the charge as to be transported.[13] These values are in agreement with the literature reports for diamond films.[4]

In Fig. 2 a typical room temperature Raman spectrum taken with the He–Ne laser is shown. When the He–Ne laser is used the contributions from nondiamond phases are enhanced.[3] Therefore this excitation energy is more convenient to study the quality of the film. Moreover, besides the Raman spectra, the Si related luminescence (SiL) is easily observed, corresponding to an energy of 1.68 eV of the ZPL. Spectra have been taken in different regions of the slab, both in the front (F) and the back surface (D). In order to estimate the quality of the film, we have determinated the ratio of integrated intensity of the 1332 cm^{-1} diamond band to the total integrated intensity of the Raman spectrum between 1100 and 1700 cm^{-1}. This ratio gives a figure of merit (FOM).[3] This value, expressed as a percentage, gives a measure of the ratio of diamond and nondiamond carbon phases. The results obtained agree with the values found for CVD films in previous work.[3,14]

Figure 3 plots the distribution of diamond Raman line intensity (DRI), line width [full width at half maximum (FWHM)] and ratio of diamond Raman to nondiamond Raman intensities (FOM) in the corresponding regions of front and back surfaces. It can be seen that these parameters are unevenly distributed along the sample. In order to determine the correlation between the different parameters we studied plots of DRI versus FWHM, FWHM versus FOM have been made, as shown in Fig. 4. In the same figure plots of SiL

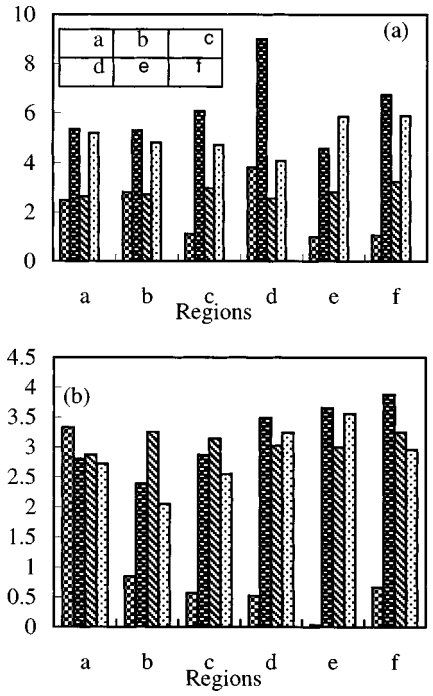

FIG. 3. Distribution of diamond Raman line (DRI); line width (FWHM); ratio of diamond and nondiamond Raman intensities (FOM); Si emission intensity (SiL): (a) F face; (b) D face. (checkered pattern) FOM (white dotted pattern) DRI (arb.un) (diagonal zig–zag pattern) FWHM (cm^{-1}) (black dotted pattern) SiL (arb.un).

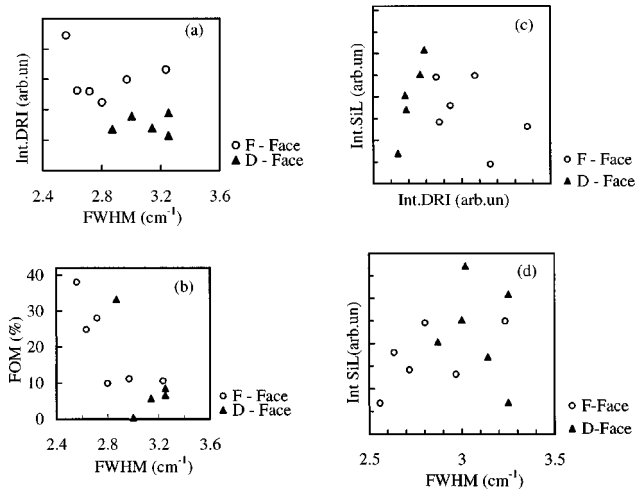

FIG. 4. (a) Plot of DRI vs FWHM; (b) plot of FWHM vs FOM; (c) plot of SiL vs DRI; (d) plot of SiL vs FWHM.

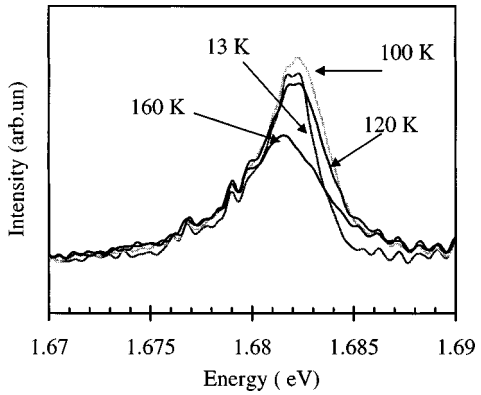

FIG. 5. Photoluminescence emission spectrum.

intensity versus DRI and SiL versus FWHM are shown. There is an overall increase in quality, as expected from the back to the front face. In both faces there is a fair correlation between FWHM and FOM, implying that the presence of nondiamond phases causes random stresses in the diamond phase as shown by the line broadening. However no correlation is found between these parameters and DRI. This clearly indicates that we must be very careful when attributing film quality to only one of these parameters. We may have a large amount of diamond film but the grains have grown with larger internal strain, which gives large FWHM. Also a good quality grain may be embedded in large nondiamond phases bringing about a bad value for FOM.

The SiL data is more complex to examine. As is shown in Fig. 4, the SiL correlates with DRI in face D, where an increase in DRI is accompanied by an increase in SiL, but in face F there is no such correlation. This indicates that the mechanism of diffusion is quite complicated. More than a simple diffusion through the diamond lattice the silicon diffuses preferentially along the grain boundaries and the nondiamond phases. Thus larger crystals will have less Si incorporated. Crystals with high SiL were expected to have larger FWHM, as the Si incorporation in the lattice brings internal strains. While such correlation is approximately observed in face F, in face D this correlation is not found. This can be explained as there are more factors affecting the crystal quality, as lattice mismatch with the substrate in the back surface. The smaller grain size and lower FOM values in the face D are clear indication of this fact.

As it wasn't possible to use the micro-Raman setup to study the behavior of the luminescence line with the temperature, the silicon related emission has been studied employing PL spectroscopy between 10 and 300 K. Consequently, spatial resolution is lost and the results have to be regarded as a mean value of the luminescence of the whole sample. The ZPL region can be seen in Fig. 5. The line is asymmetrical and shifts towards higher energies with increasing temperature from 11 until 100 K. While this shift can be explained according to the thermalization of energy levels of Si–V[5] the ZPL shifts towards lower energies, observed above 100 K can hardly be due to the decrease of the band gap with the increase of temperature. As we are dealing with deep centers, their levels are not sensitive to the band states. Indeed this effect has not been observed in deep centers in diamond (e.g., *N*3, *H*3, GR1), where a shift towards lower energies with temperature is mainly due to vibronic coupling and lattice thermal expansion. This shift between 77 K and room temperature in a center like *N*3 is of 2 meV.[15] A smaller shift was to be expected in a center like the Si–V as it has a weaker phonon coupling than *N*3.[10] Taking into account that the population of higher energy levels with temperature is opposite to the vibronic coupling, should be expected a rather small shift to lower energies. In fact it is of 3 meV between 150 and 300 K.

These data together with the asymmetric line shape and its change with temperature suggest that we consider the line as being due to the presence of two optical centers very close in energy. This situation is common in diamond, as optical centers in the same spectral region have been identified with different vibronic coupling. A typical example is the case of *S*3, *H*3, *e*3*H* centers,[16] all occurring within 1 meV, but with different phonon coupling, different life time, different excitation spectra, and different temperature dependence. Also close to *N*3 there is a center occurring at 417 nm, in both natural and synthetic diamond,[17] that in earlier work has been assumed as a distorted *N*3.[18]

To test this hypothesis the luminescence line was deconvoluted into a line at 1.679 eV (attributed to an *X* center) and two lines at 1.682 and 1.683 eV, that can be regarded as the envelopes of the dominating emission of Si–V defect. The results are shown in Fig. 6 for 10 K.

It is to be noted that also previous work[19] deconvoluted the emission line, at 77 K, with a Gaussian at 1.681 eV and a Lorentzian at 1.679 eV, but the authors attributed the asymmetry to a different silicon concentration in the film. It is interesting to note that the value of the 1.679 eV for the peak energy has been reported previously for the Si center.[7] In this work the quenching parameters are also different from the values given for films where the line is close 1.681 eV.[8,10] This supports the idea that two different centers may be present in diamond films.

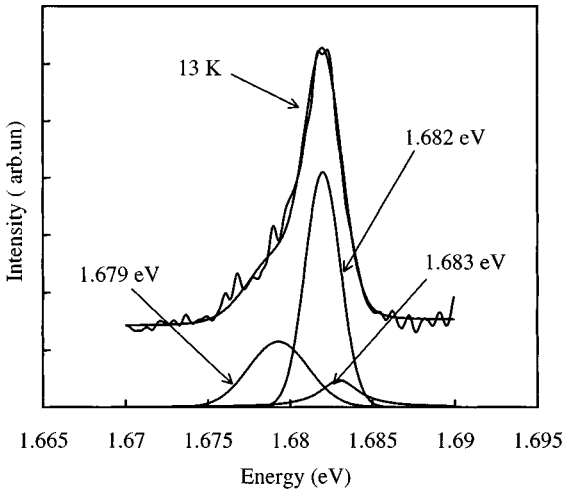

FIG. 6. Photoluminescence emission intensity of: (a) 1.68 eV system; (b) 1.679 eV system.

In Fig. 7 we plot the intensity of Si–V and *X* center versus temperature. The overall shift in energy can be attributed to the different relative intensities of the two emissions with temperature. In order to explain the results we assume that there are, for the two centers, a direct excitation path and an indirect one through a trap that accounts for the increase in luminescence intensity between 15 and 30 K for the Si–V center and 120 and 180 K for the *X* center. This is in agreement with the presence of two decay times for the Si–V center of 3 ns and 100 ms.[20] According to this model the intensity of one center will be given by

$$I_1=[I_f+I_sW_1/(W_1+W_2)]\cdot W_r/(W_{\rm rl}+W_{\rm nrl}),$$

where I_f is the intensity of the direct emission, I_s the intensity of the emission arising from the trap, W_1 and W_2 are the temperature dependent transition probabilities from the trap to the two centers, and W_r and $W_{\rm nr}$ are the radiative and nonradiative transition probabilities from the excited state of the center considered. A similar equation holds for the other center, exchanging indexes 1 and 2.

Nonradiative transitions, as the transition from the trap to the excited levels of the centers, occur via vibronic interactions. Two main mechanisms are commonly observed: a classical over a barrier transition, where the transition probability W is given by Mott equation: $W=W_0\exp(-E_a/kT)$ with E_a the activation energy, and a tunneling process given by $W=C(kT^*)^{-1/2}\exp(-E_a/kT^*)$, where T^* is the effective phonon temperature.[21]

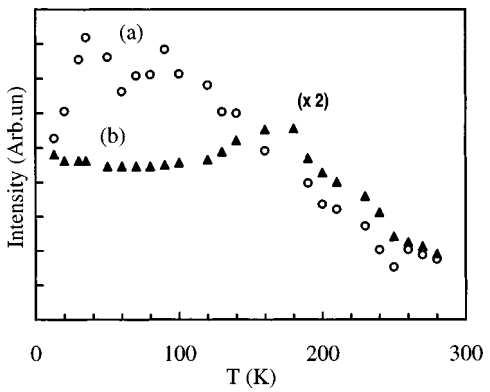

FIG. 7. Temperature dependence of the photoluminescence emission intensity of: (a) 1.68 eV system; (b) 1.679 eV system.

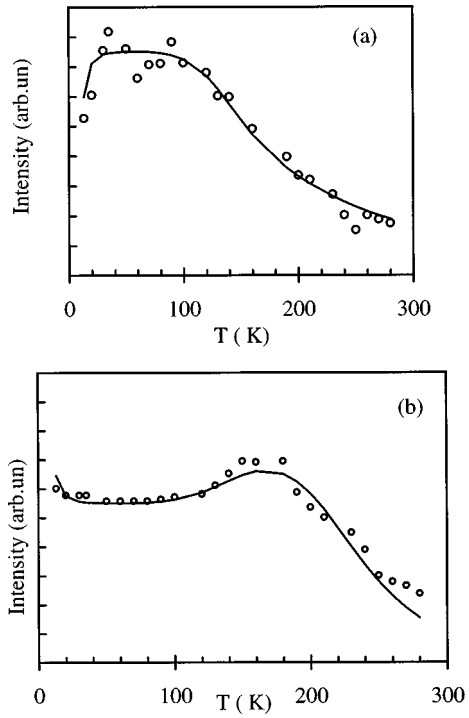

FIG. 8. The fit to the experimental data: (a) 1.68 eV system; (b) 1.679 eV system.

A best fit to the experimental data has been obtained assuming a classical transition from the trap to the Si–V center, with an activation energy of 6 meV [Fig. 8(a)]. The transition to the *X* center follows the tunneling mechanism, with an activation energy of 248 meV [Fig. 8(b)]. The small value of the activation energy justifies that in the temperature range studied the first transition has reached already the classical regime, while the other is mainly a tunneling process. This compares with the nonradiative transitions of the *N*3 center where the tunneling takes place for an activation energy of 566 meV.[22] For the nonradiative processes the values reported in the literature have been used.[8,7] These results agree with other reports, where a blue shift is founded in samples with low residual stress.[8]

When we compare the emission from D and F faces at room temperature, observed in the Raman spectroscopy, we see that at F face the line is broader and less intense. In order to explain this we have to take into account that the two emissions have different thermal quenching parameters, the Si–V being quenched faster. Thus we must expected that Si–V luminescence at room temperature will be been only in regions where the Si–V is most intense. If the Si–V is grown preferentially on F face the results can be explained. At D face we will have mainly *X* center emission, and so we have an intense and narrower line. At F face we will have still emission from Si–V at room temperature. Thus in that face we observed a mixture of the two emission and therefore the line becomes broader and shift slightly to higher energies as

indeed has been observed. Also the fact that the position of the emission is reported at lower energies when the films have poor quality[7,6] can now be explained. Therefore we assume that Si–V dominates on the regions where best diamond film is present and *X* center occurs mainly at the first stage of growth.

IV. CONCLUSIONS

Even high quality diamond films present heterogeneities at the micron scale both along the growth direction and in a growth plane. At the back surface more nondiamond phases are observed, accompanied by a broader Raman line. Absolute intensity of the diamond peak is however not correlated with a good quality as assessed by the Raman line width and the ratio of this line to the nondiamond Raman lines. Also the silicon related luminescence intensity that can be correlated with the diamond line intensity in the back face, shows no correlation in the front face, suggesting that the migration of the silicon in the diamond film follows a complex pattern, being more favorable along grain boundaries.

The luminescence data indicate that the emission observed around 1.68 eV can be attributed to two different centers, partially populated from a trap. This explains previous observations on the luminescence in this region and accounts for the red shift observed in the emission for higher temperatures.

The conjugation of the results of luminescence and micro-Raman, indicated that the Si–V optical center is associated with ''high quality'' and the *X* center with ''low quality'' CVD diamond films.

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